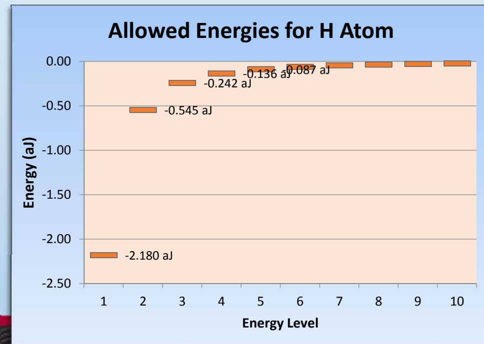
Why did it take over 60 years for scientists to explain the atomic emission spectrum of Hydrogen? Why do we expect our students to understand the explanation in 30 minutes or less?

>60 y



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How should the atomic emission spectrum of hydrogen fit into the larger story of the atom?

My plan:

- Brief overview of historical path to discovery with emphasis on work of Niels Bohr.
- How is Bohr's work treated (or mistreated) in textbooks?
- An alternate approach to consider.

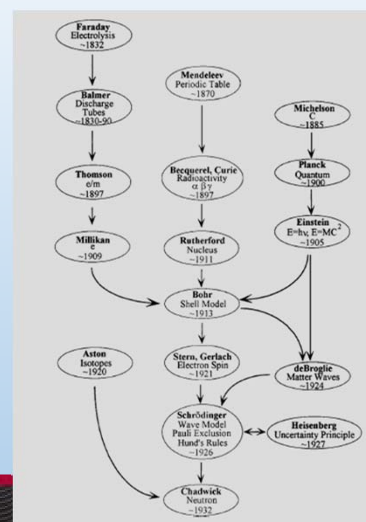

Figure 1. The Modern Atom: a flow chart of major theoretical and experimental contributions (who, what, and when).

Leary, J.L.; Kippeny, T.C. *J. Chem. Educ.* **1999**, 76, 1217-1218

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The Path to Discovery

- ~1859 — Observation of discrete emission (line spectra) from gas discharge tubes
- 1885 — Balmer's equation
- 1888 — Rydberg's equation
- 1901 — Plank accounts for black body radiation in terms of light quanta: $E=\tau h\nu'$
- 1905 — Einstein accounts for the photoelectric effect in terms of light quanta: $E_{photon} = h\nu$
- 1911 — Rutherford's nuclear model of the atom.
- 1913 — Bohr's model of the hydrogen atom with discrete energy levels.
- 1926 — Wave equation derived and solved for the hydrogen atom. (Schrödinger)

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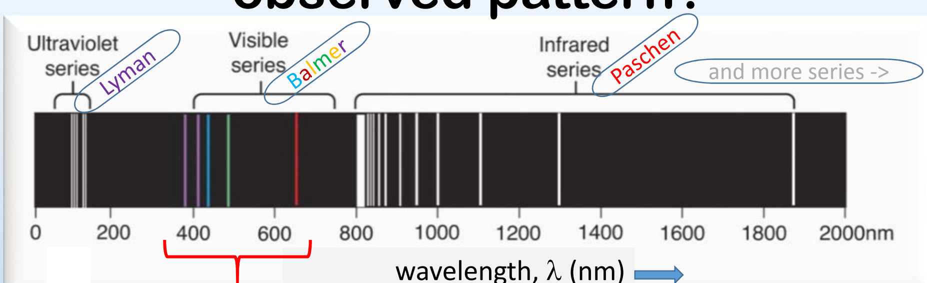
Why are only specific wavelengths emitted in an observed pattern?



Balmer's equation:

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Rydberg Equation:

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

$m, n = 1,2,3,4\ldots$ and $n > m$

Difference between two terms

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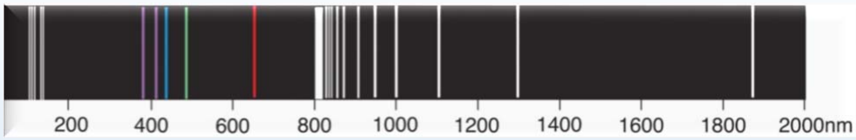

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

What was missing?

According to classical physics the energy of light is related to the intensity (wave amplitude), and not the wavelength or frequency.

But this changed:

- Planck (1901), from his study of blackbody radiation, concluded the energy of the emitted light is quantized according to: ***E=τhν'***, *where* ***ν'*** is a frequency of oscillation ('an atomic vibrator'), ***h*** is a constant, and ***τ*** is a positive integer *1,2,3…*
- Einstein (1905), from his study of the photoelectric effect, concluded that the energy of a single light particle is proportional to the frequency of the light according to: $E_{photon}=h\nu$

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Bohr's planetary model of the atom

1 $F_{electrostatic} = F_{centripetal\ accel.}$ {provides

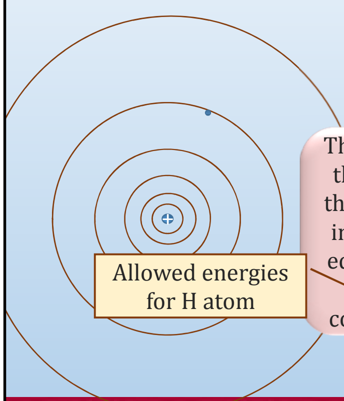
Bohr applied Planck's equation for blackbody radiation to the light emitted by excited hydrogen to forge a workable link between light frequency and energy.
(Bohr related the frequency of emitted light to the frequencies of revolution for the orbiting electron before and after emission.)

2 Conservation of Energy

3 Planck

$$\Delta E_{atom} = E_{emitted\ light} = \tau h\nu$$

The connection between the ΔE of the atom and the "difference in terms" in the Balmer/Rydberg equation was suggested by a spectroscopist colleague, H.M. Hansen.



Allowed energies for H atom

$\tau^2 h^2$ where $\tau = 1, 2, 3\ldots\infty$

Derived consequence:

$$mvr = \frac{\tau h}{2\pi}$$

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How is Bohr's work treated (or mistreated)* in textbooks?

A. "Rigorous approach" (still used in P. Chem. & Ph

$F_{es} = F_{ca}$ {stable orbit}

&

$$mvr = \frac{\tau h}{2\pi}$$

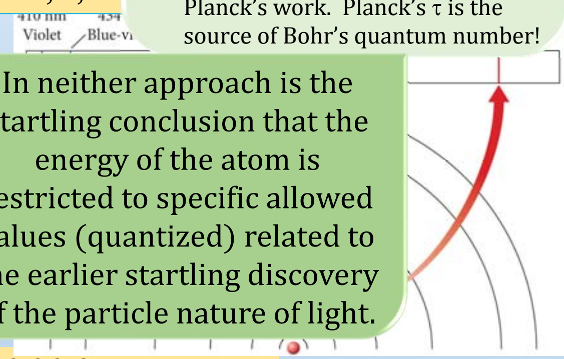
Reconstructed derivation!

$$E_n = -\frac{e^4 m_e}{8\varepsilon_o^2 n^2 h^2}$$

$$where \;\; n = 1, 2, 3..$$

The reconstructed derivation is problematic:

1. There is no apparent justification for the angular momentum assumption other than it leads to an expression that correctly predicts emission wavelengths.
2. It also ignores Bohr's use of Planck's work. Planck's τ is the source of Bohr's quantum number!



B. "Modern approach"

- present a simplified equation without derivation $E_n = \frac{-2.18\times10^{-18} J}{n^2}$
- relate observed emission lines to transitions between allowed states or orbits

In neither approach is the startling conclusion that the energy of the atom is restricted to specific allowed values (quantized) related to the earlier startling discovery of the particle nature of light.

* See Haendler, B.L. Presenting the Bohr Atom. *J. Chem. Ed.* 1982,59 (5),372-376.

Is there a more direct and compelling connection between atomic line spectra and the quantization of an atom's energy?

For simplicity and improved rigor:

- Separate the two problems that Bohr was trying to solve:
  - i. Where is the electron in the hydrogen atom and what is it doing?
  - ii. Why do excited hydrogen atoms emit only specific wavelengths of light?
- First, demonstrate rigorously that the line spectrum of hydrogen requires that the energy of the atom be quantized, and derive an equation for the allowed energies.
- Then follow-up with the question of electron arrangement and behavior (Bohr & DeBroglie), and then the deeper question of why must the energy be restricted to discrete values (Schrödinger et al).

Rittenhouse, R.C. Understanding Atomic Structure: Is There a More Direct and Compelling Connection between Atomic Line Spectra and the Quantization of an Atom's Energy. *J. Chem. Educ.* 2015, **92**, 1035-1039.

The implications of the hydrogen line spectrum – a more direct, yet rigorous, approach.

1. Starting point: Balmer/Rydberg empirical equation

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \text{ where } m, n = 1,2,3,4\ldots \text{ and } n > m$$

2. Use Einstein's equation from his explanation of the photoelectric effect to rewrite the Rydberg equation in terms of photon energy:

With $E_{ph} = h\nu = \frac{hc}{\lambda}$,

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \text{ where } R_\infty \text{ is } 1.097 \text{ X } 10^7\,\text{m}^{-1} \text{ and } m, n = 1,2,3,4\ldots \text{ with } n > m$$

becomes $E_{ph} = \frac{hc}{\lambda} = hcR_\infty\left(\frac{1}{m^2} - \frac{1}{n^2}\right) = \frac{hcR_\infty}{m^2} - \frac{hcR_\infty}{n^2}$

The two terms have units of energy

Continued…

$$E_{ph} = \frac{hcR_\infty}{m^2} - \frac{hcR_\infty}{n^2}$$

3. Apply energy conservation for emission: $E_{photon} = \Delta E_{atom} = E_{initial} - E_{final}$
   - Assign the corresponding energy terms in the rewritten Rydberg equation to:

$$E_{initial} = \frac{hcR_\infty}{m^2} \qquad E_{final} = \frac{hcR_\infty}{n^2}$$

4. What type of energy are we talking about? What kind(s) of energy would be expected to exist in a hydrogen atom with a positive nucleus and an electron?
   - If electrostatic potential energy dominates, then energy terms must be negative. $E_P = k\frac{Q_{p^+}Q_{e^-}}{r}$
   - What can be done to get a difference between two negative terms?

$$E_{ph} = \frac{hcR_\infty}{m^2} - \frac{hcR_\infty}{n^2} \Rightarrow E_{ph} = \frac{-hcR_\infty}{n^2} - \frac{-hcR_\infty}{m^2}$$

   - Then with conservation of energy

$$E_{initial} = \frac{-hcR_\infty}{n^2} \text{ and } E_{final} = \frac{-hcR_\infty}{m^2} \text{ with } n, m = 1,2,3\ldots \text{ and } n > m$$

5. Finally, generalize

$$E_n = \frac{-hcR_\infty}{n^2} \text{ with } n = 1,2,3\ldots\infty$$

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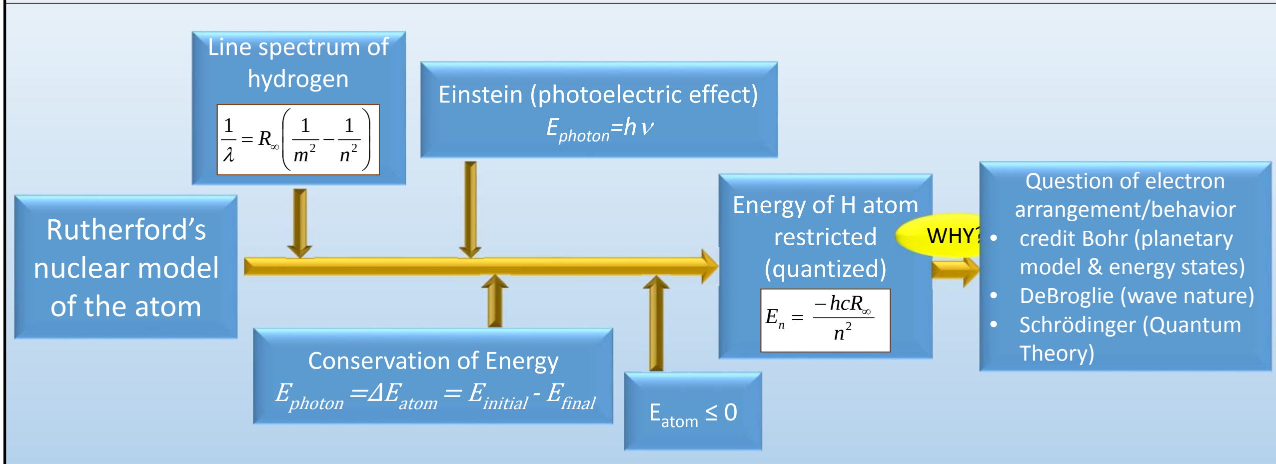

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